EMSP
Environmental Management Science Program
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VADOSE AND SATURATED ZONE CHARACTERIZATION, MONITORING, MODELING, AND ANALYSIS

PRECISE, ACCURATE LOCATION OF CONTAMINANTS AND RELIABLE ESTIMATES OF FUTURE MIGRATION PATHWAYS ARE ESSENTIAL FOR COST-EFFECTIVE REMEDIATION

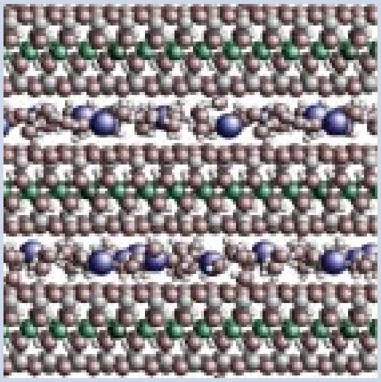
Subsurface characterization problems are particularly acute for the U.S. Department of Energy (DOE) because contaminants are located from near the surface to deep in the subsurface, in arid and wet climates, and in almost every possible geologic matrix. The first requirement for environmental remediation of subsurface contaminants is that their precise location be determined. Secondly, reliable estimates of future migration of the contaminants must be made so that remediation priorities can be established appropriately. The projects discussed here are related to these two goals.

The projects, described in more detail on the following pages, include:

- two approaches to assessing the importance of interfacial processes to the transport of organic materials in the subsurface;
- improved electrochemical methods for determining the concentration of uranium and chromium, laser-induced breakdown spectroscopy (LIBS) for remote measurements of trace metals, and methods to improve sensitivity of simple detectors for organic compounds;
- applications of modern molecular biology techniques to develop methods to monitor the presence of microbes capable of degrading hazardous organic compounds;
- development of computer codes to use data simultaneously from several geophysical techniques for subsurface characterization, improvements in methods for surface wave seismic data inversion to obtain tomographic geometry, new computational and experimental methods for measuring the ease of fluid movement through soil, and use of nuclear magnetic resonance (NMR) imaging for locating water in the subsurface; and
- studies of the mechanisms by which plutonium can migrate in the subsurface, an investigation of the effectiveness of certain clays as sealing buffers to prevent radionuclide transport out of geologic repositories, new techniques for measuring migration of small amounts of radionuclides, and the role of colloids as carriers of several hazardous metal and radionuclide species.

Analytical Determination or Characterization of Contaminants

This computer simulation, provided by a New Mexico State University project (54823), illustrates a hydrated Cs-smectite clay mineral. The project goal is to investigate the molecular origin of the binding of ions, particularly cesium(I) and strontium(II), to clays. The team has developed a computer simulation code for investigating hydrated smectite and vermiculite clay interactions with various ions.



PROBLEMS/SOLUTIONS

- The current understanding of the mobility of contaminants is inadequate to support cleanup, closure, or performance assessment. EMSP studies of colloidal transport mechanisms and soil fixation/binding mechanisms are directly related to high-priority needs cited at Hanford, Oak Ridge, and other DOE sites.
- Needs for post-closure monitoring instrumentation will become even more important for long-term performance assessments. Several projects are directed toward developing new analytical instrumentation that can be used for long-term monitoring, such as down-well uranium monitoring at Uranium Mill Tailings Remedial Action sites.
- The safety of geological repositories for long-term storage of high-level waste is often doubted. One project is investigating interactions of radionuclides with the minerals that may be present in the vicinity of such repositories so that predictions of future containment may be made more reliably.
- Bioremediation appears to be the most appropriate technique for cleanup of hazardous organic compounds deep in the subsurface, i.e., 100 feet at the Pantex Plant, but reliable methods are needed to monitor the presence of the appropriate microbes. Techniques being developed by EMSP projects could replace the current cumbersome and expensive procedures.

ANTICIPATED IMPACT

- The cost savings for each well that does not have to be drilled because of improved characterization by geophysical techniques is $10,000 to $20,000.
- Improved methods for nonintrusive detection of buried waste sites would meet high-priority needs cited at most major DOE facilities, such as the Oak Ridge National Laboratory waste areas and Y-12 burial grounds, the Hanford 100, 200, and 300 areas, and the low-level radioactive waste disposal facility at Savannah River Site (SRS).
- As noted in an SRS need statement "a simple method of determining hydraulic conductivity...has numerous applications at the SRS (Saltstone, for example) and other DOE sites." Developing such a method is the goal of one project.

Models for Subsurface Flow

The University of Notre Dame and coworkers team is assessing the importance of interfacial processes to multiphase flow. Their work involves theoretical derivation of equations based on conservation principles, lattice Boltzmann modeling of hydrodynamics, and solution of field-scale equations using numerical methods to assess the complete theory. The ultimate goal is improved modeling of the transport of organic materials in the subsurface.

Determining the relationships among capillary pressure, saturation, and interfacial areas is the objective of the Cornell University and coworkers project. The team is working to integrate the theory, experiments, and numerical simulations into a coherent approach to study the role of interfacial areas in porous media flow physics. The photoluminescent volumetric imaging experimental technique has been critical to the validation of the theoretical models. The ultimate goal is to use the results of this research to generate site specific soil moisture characteristic surfaces.

Analytical Determination or Characterization of Contaminants

The New Mexico State University (NMSU)/Pacific Northwest National Laboratory (PNNL) project (54639) has been focused on developing a miniaturized electrochemical sensor for uranium and chromium at parts per billion (ppb) concentrations. A submersible probe for these two metals has been studied, with the goal of producing an inexpensive probe that can be left in a well, for example, to monitor metal concentrations at ppb levels without expensive sampling and laboratory analyses. This probe incorporates a microdialysis sampling procedure that may enable in-situ sensing of metal speciation.

The Lawrence Berkeley National Laboratory team has investigated methods to use DNA-based procedures for the detection of a naphthalene-degrading gene. They have used a peptide nucleic acid probe to identify a polymerase chain reaction (PCR) product from a naphthalene-degrading organism. Matrix-assisted-laser-desorption-ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was found to offer the possibility for automation with rapid detection, which is needed to track the course of bioremediation over large polluted areas.

The Pacific Northwest Consortium team is building a beamline to access the Advanced Photon Source at Argonne National Laboratory. This facility will make an intense, spatially resolved x-ray source available for x-ray absorption spectroscopy for conducting basic research on topics such as chemical speciation of tank wastes, radiation-induced structural changes in waste forms, and verification of modeling for transport of contaminants under geologic conditions.

A rapid screening method to determine a contaminated site's potential for microbial bioremediation is the objective of the Oak Ridge National Laboratory (ORNL)/University of Washington project (55108). They have been able to amplify relatively short segments from the DNA of a bacterial enzyme that can oxidize trichloroethylene. They then use a mass spectrometry technique capable of detecting these segments to determine whether the microbes were present in the original sample. These new methods could replace current laboratory-based methods that are cumbersome and expensive, and they could lead to a more robust way to determine whether bioremediation for a particular contaminant can occur.

Models for Subsurface Flow

The University of Notre Dame team (54576) is assessing the importance of interfacial processes to multiphase flow. Understanding of water flow or infiltration in a relatively dry surface soil (top) must be derived from analyses that consider fluid movement between the intricate network of pores and solids of the soil (middle).

When a laser pulse is focused on a surface, a small amount of the surface can be vaporized with sufficient energy to cause ionization of the vapor with resulting light emission characteristic of the vaporized species. The University of South Carolina team is studying LIBS using fiber optics for remote measurements of trace metals. They have performed the first demonstration of LIBS imaging using fiber optics and have combined LIBS and Raman spectral imaging in a single probe. The goal is to develop reliable, field-deployable instruments to reduce dependency on laboratory analyses.

The University of Tennessee/ORNL team (55328) has been investigating new techniques for detecting a wide variety of organic molecules. Electron capture with the resulting formation of negative ions is widely used in sensitive but inexpensive detectors for highly chlorinated organic compounds; however, this technique does not work with most organic species. It has recently been discovered that the formation of negative ions is enhanced by up to a hundred thousand times if the molecule is in a highly-excited state. Molecules can be produced in these highly excited states by laser excitation or in a glow discharge. Efficient formation of negative ions in benzene and toluene was observed, and it was found that weak electric and magnetic fields further enhance ion formation.

Methods for Subsurface Site Characterization

The University of California/Stanford University project goal has been the joint use of seismic and electromagnetic data for subsurface characterization of a Superfund site at Lawrence Livermore National Laboratory (LLNL). The team has interpreted vertical seismic profile (VSP) and electromagnetic survey data, identifying three anomalies believed to represent the presence of gases below the water table. Knowledge of how seismic and VSP velocities are affected by variations in rock formations and by pore fluid saturation is important for reliable characterization.

The New Mexico Institute of Mining & Technology/Blackhawk Geometrics team (54857) is investigating a surface NMR technique for imaging water distribution in the subsurface. They have found that NMR measurements can determine water distribution in coarse-grained aquifers, i.e., formations from which water can be readily withdrawn. However, use of the technique is hindered by power lines, the presence of minerals with high magnetic susceptibility, and an inability to detect water in fine-grained sediments.

One LLNL team (54950) has constructed a vadose-zone observatory to obtain better understanding of vadose zone transport processes. Plume-tracking techniques include electric resistance tomography, monitoring wells at multiple depths, and sensors for detecting changes in saturation, temperature, and pressure. Plume release experiments showed that transport to the groundwater occurred rapidly, and the team concluded that the importance of heterogeneity and “fast paths” for understanding the transport of contaminants to the water table makes two-dimensional models of layered soils inadequate for evaluating transport processes. They propose that dynamic characterization experiments and diagnostic modeling are the best methods to anticipate contaminant transport.

The hydraulic conductivity must be known in order to estimate the transport rate of many contaminants from the surface to the water table. The primary objective of the New Mexico Institute of Mining & Technology/Sandia National Laboratory (SNL) project (55109) is to design and test new permeameters to measure widely varying conductivities at different sites. The team’s early work focused on mathematical techniques for analyzing permeameter data. They also evaluated the effect of permeameter measurement errors on estimated spatial statistics, and suggest that in some cases it may not be possible to directly measure some hydraulic properties for use in spatial analysis. These results are being used in the design of new permeameters, for which field tests are being planned.

The Georgia Institute of Technology/ORNL team (55218) is developing surface-wave tomography field and laboratory techniques for characterizing near-surface structures such as those associated with the burial of wastes. An analysis of seismic data from the ORNL K-901 burial site showed that more field data were needed because the instruments recording the signals were insufficiently sensitive at frequencies below 8 Hz. A newly designed data acquisition software system was used to obtain data from four sites with different surface velocity characteristics and with some known subsurface structures so the new techniques could be evaluated. The primary remaining task is to refine the mathematical techniques for surface-wave seismic data inversion to obtain tomographic geometry.

Project Teams

Lead Principal Investigator (Award Number)

- University of Notre Dame
  PI: William G. Gray (54576)
  Lawrence Livermore National Laboratory
  Los Alamos National Laboratory
- New Mexico State University
  PI: Joseph Wang (54639)
  Pacific Northwest National Laboratory
- University of California – Berkeley
  PI: Yoram N. Rubin (54655)
  Stanford University
  Lawrence Livermore National Laboratory
- Woods Hole Oceanographic Institute
  PI: Ken O. Buesseler (54683)
  Pacific Northwest National Laboratory
- Lawrence Berkeley National Laboratory
  PI: W. Henry Benner (54698)
- Cornell University
  PI: Carlo D. Montemagno (54793)
  Princeton University
  University of Notre Dame
- Pacific Northwest Consortium –
  Collaborative Access Team:
  University of Washington
  PI: Edward A. Stern (54800)
  Pacific Northwest National Laboratory
  Simon Fraser University
- New Mexico State University
  PI: David E. Smith (54823)
- New Mexico Institute of Mining & Technology
  PI: Jan M. H. Hendrick (54857)
  Blackhawk Geometrics
- Massachusetts Institute of Technology
  PI: Philip M. Gschwend (54888)
- Lawrence Livermore National Laboratory
  PI: Charles R. Carrigan (54950)
- Oak Ridge National Laboratory
  PI: Michelle V. Buchanan (55108)
  University of Washington
- New Mexico Institute of Mining and Technology
  PI: John L. Wilson (55109)
  Sandia National Laboratory – Albuquerque
- Lawrence Livermore National Laboratory
  PI: Gregory Nimz (55148)
- University of South Carolina
  PI: Scott Goode (55205)
- Georgia Institute of Technology
  PI: Timothy L. Long (55218)
  Oak Ridge National Laboratory
- California Institute of Technology
  PI: G. J. Wasserburg (55284)
  Texas A&M University
- University of Tennessee
  PI: Lal A. Pinnaduwage (55328)
  Oak Ridge National Laboratory
- Sandia National Laboratory
  PI: David L. Alumbaugh (55332)
  University of Arizona
- Lawrence Livermore National Laboratory
  PI: Patricia A. Berge (55411)

Office of Science & Technology
Office of Environmental Management
U.S. Department of Energy

Subsurface characterization by any single geophysical technique is usually ambiguous. The SNL/University of Arizona team (55332) will develop computational codes to combine information from electric resistivity tomography (ERT) surveys and heterogeneity/hydrologic processes with other hydrologic data, such as pressure and moisture content. A characterized test site being built in New Mexico has 13 wells providing access for an array of geophysical probes. A grid of ERT electrodes was installed, and characterizations of samples collected during drilling were completed. Infiltration of water and salt will be used to test the ability of the codes to reconstruct the known subsurface structure.

Improved underground imaging is also the goal of another LLNL project (55411). These investigators are developing algorithms relating geophysical measurements to hydrogeological properties. After performing laboratory measurements of elastic and electrical properties of sand-clay and sand-peat mixtures at low pressures, the team explored theoretical and empirical methods for relating the measured properties to porosity and soil composition. Results were compared to available geophysical field data, and recommendations were made for improving the design of geophysical field experiments at contaminated sites. A new EMSP project will continue this work, using Hanford vadose zone cores and sediments.

Migration of Contaminants

The Woods Hole Oceanographic Institute/PNNL project (54683) is designed to study speciation of plutonium and its association with dissolved organic complexes in water. They have found that most of the Pu in the SRS groundwater is in highly oxidized forms that are less associated with colloids and significantly more mobile than previous data would imply. The increase of the $^{240}Pu/^{239}Pu$ ratio downstream of the plume occurs because ^{240}Pu is produced from a more mobile curium precursor and because of its enhanced mobility in the oxidized form.

A key feature of geological repositories for long-term storage of nuclear wastes is use of certain clays as backfill material to provide a sealing buffer to radionuclide transport. One NMSU project (54823) is investigating the molecular origin of the binding of ions, particularly cesium(I) and strontium(II), to clays. Because fundamental understanding of clay behavior is essential to predict migration of radionuclides in clay-rich soils, this team has developed a computer simulation code for investigating hydrated smectite and vermiculite clay interactions with various ions.

Pollutants adsorbed onto immobile solids in an aquifer cannot be removed by pump-and-treat technologies. However, if clays, iron oxides, and other sorbents could be dispersed into colloidal-size particles, it might be possible to pump them out along with their adsorbed contaminant. The Massachusetts Institute of Technology team has chosen a chromium-contaminated aquifer to explore this strategy. They characterized the site to identify the level of chromium contamination and the minerals in the sediments. Laboratory experiments with materials designed to mobilize colloids were performed, and citrate solutions at a pH of 5.5 or higher were found to remove about half of the sediment chromium. Single well injection-withdrawal experiments are planned to determine the effect of colloid mobilization solutions on aquifer materials.

Low concentrations of long-lived radionuclides are difficult to measure using counting techniques. One LLNL team (55148) is studying radionuclide migration using accelerator mass spectrometry (AMS), a highly sensitive technique available at about 40 sites worldwide. They developed the first AMS procedures for measuring technetium-99 with detection limits from 10 to 100 femtograms. In addition, determinations of isotopes of iodine and chlorine can be done at levels below those achievable with other techniques. It is thus possible to investigate radioactive species migration without using hazardous samples that cause disposal problems. This will allow more reliable estimates of migration at highly contaminated sites.

The California Institute of Technology/Texas A&M University team has used counting and mass spectrometry techniques to investigate fundamental controls on naturally occurring uranium, thorium, radium, and radon isotopes in the subsurface. The goal is to use this information to predict migration rates for nuclear-waste radionuclides. After collecting samples from Brookhaven National Laboratory monitoring wells, they found that colloids are important carriers of uranium in the aquifer. A theoretical model is being developed to describe the transport of U, Th, Ra, and Rn in the zone above the water table and within the aquifer.

For additional information about the EMSP, please contact one of these representatives:

Mark A. Gilbertson
Director, Office of Science & Risk
(202) 586-7150
emsp@id.doe.gov
www.em.doe.gov/science

Tom Williams
EMSP Director, DOE-ID
(208) 526-2460
emsp@id.doe.gov
www.id.doe.gov/emsystems/emsp

Roland Hirsch
EMSP Director, Office of Science
(301) 903-9009
emsp@id.doe.gov
www.er.doe.gov